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Degradation of nine nitrosamines in water by ultraviolet irradiation

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ABSTRACT

Ultraviolet (UV) degradation of nine nitrosamine (NA) species was investigated. Four UV lamps were used for the experiment: a KrCl excimer lamp with an emission peak at 222 nm (222-EX); a low-pressure mercury lamp with a peak at 254 nm (LP); a filtered medium-pressure mercury lamp with the emission range narrowed to 230–270 nm by an optical filter; and an XEFL lamp with the emission range narrowed to 220–280 nm. Solutions of the nine NAs were exposed to one of the four UV lamps. Water was sampled in time series, to investigate degradation of NAs. As an overall trend, the degradation rate was slightly slower with the LP lamp than with the other lamps, especially the 222-EX. The degradation of cyclic NAs (*N*-nitrosodiphenylamine, *N*-nitrosopyrrolidine, *N*-nitroso-piperidine [NPIP], and *N*-nitrosomorpholine) was dependent on the tested lamp, and the highest degradation of NPIP was observed. Among non-cyclic NAs, degradation appeared to be faster as the carbon chain length increased from *N*-nitrosodimethylamine (NDMA) to *N*-nitroso-di-n-butylamine. Of the nine NAs, NDMA was one of the most persistent species.

Keywords: Mercury UV; Mercury-free UV; Nitrosamines; Xenon; KrCl

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1. Introduction

There is a long history of environmental pollution by nitrosamines (NAs). Initially, industrial sources were accused of polluting water mainly with *N*-nitrosodimethylamine (NDMA), which was first detected in water during the 1970s [1]. At the beginning of the twenty-first century, however, disinfection of drinking water appeared to be the main source of NAs [2], especially disinfection processes using chlorine or ozonation treatment [3], which can turn a wide variety of compounds into NAs [4]. About 90% of NAs are carcinogenic in humans [1,5]. Furthermore, NAs are polar compounds, which are usually soluble in water, and their extraction with organic solvents is difficult. They are also not adsorbed on non-polar surfaces. NAs cannot be removed from water by aeration [1]. To date, there are no effective techniques for use in the water-treatment supply chain to stop NA production in drinking water or wastewater, and there are no regulations governing NA concentrations, except for NDMA, *N*-nitrosodiethylamine (NDEA), and *N*-nitroso-di-*N*-propylamine (NDPA) in California [6] and NDMA in Ontario, Canada [7].

NAs in water have been investigated widely in many countries, including Canada [7], the United States [6,8], Japan [9–11], the United Kingdom [12], Korea [5], and China [4,13]. In China, NAs have been detected at a range of concentrations, including NDMA (range 6.4–13.9 ng/L), NDEA (1.9–16.3 ng/L), *N*-nitroso-di-n-butylamine (NDBA; 1.0–19.9 ng/L), *N*-nitrosomorpholine (NMOR; 1.1–2.8 ng/L), *N*-nitrosodiphenylamine (NDPhA; 0.6–2.9 ng/L), and *N*-nitrosomethylethylamine (NMEA; 1.0–1.2 ng/L) [4]. In the Jialu River basin, China, high concentrations of NAs were found because there are no water treatment plants; untreated industrial waste enters the river, and the population near the industrial complex uses the river water as drinking

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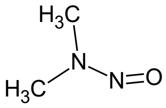
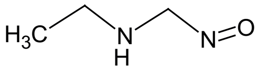
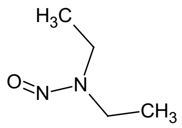
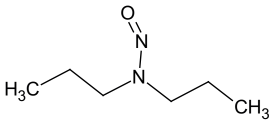
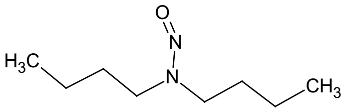
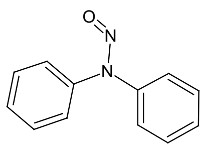
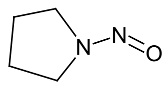
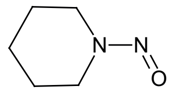
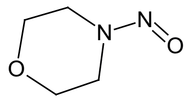
water [13]. The maximum concentrations of NDMA, NDEA, and NDBA found were 22.5, 68.4, and 15.8 ng/L, respectively. In Korea, analysis of water from the Nakdong River next to an industrial complex detected NDMA, NMEA NDEA, NDPA, NDBA, and NDPhA, with the last three appearing in August with the increase in water temperature [5].

In the United States, a study showed that NDMA, but not NMOR, is a by-product of water treatment involving chloramine disinfection [8]. These two NAs were frequently detected in the treated wastewater before chlorine was added. The NDMA concentrations ranged from not detected (ND) to 34 ng/L (median level = 8.5 ng/L) and those of NMOR from ND to 12,700 ng/L (median level = 17 ng/L). Other NAs increased with chloramine disinfection, including NDEA (3–30 ng/L), *N*-nitrosopyrrolidine (NPYR; 8–22 ng/L), and NDPA (3.4 and 4.1 ng/L in two wastewater treatment plants). In Japan, NDMA is the main NA expected, and a national survey found NDMA concentrations of up to 4.3 ng/L in raw water, and in the Yodo River basin drinking water treatment plant; the highest NDMA detected at 20 ng/L after ozonation [9–11]. Moreover, NMOR was detected in untreated water in Spain (2.8 ng/L), and in river water in Germany and France (92–114 ng/L) [13]. In the United Kingdom, NA concentrations after water treatment plants were very low or undetectable [12]. Generally, NDMA and NDEA are the predominant NAs measured, with concentrations up to 730 ng/L in sewage effluent [14].

Many studies have examined NDMA, and data on its concentration are easy to find, while there is little information on the other NAs. However, NDMA is not the most dangerous NA, for example, NDEA is more carcinogenic than NDMA and its maximum contaminant level (MCL) is lower than that of NDMA (Table 1). Consequently, it is necessary to study how to destroy all NAs. NAs are very sensitive to ultraviolet (UV) wavelengths between 200 and 300 nm [15].

Table 1
Basic information on the nine NAs

Nitrosamine (Abbreviation)	Formula		Molecular weight (g/mol)	MCL for R = 10^{-6} (ng/L) [6]
N-nitrosodimethylamine (NDMA)	$C_2H_6N_2O$		74.08	3
N-nitrosomethylethylamine (NMEA)	$C_3H_8N_2O$		88.11	1.5
N-nitrosodiethylamine (NDEA)	$C_4H_{10}N_2O$		102.14	1
N-nitroso-di-n-propylamine (NDPA)	$C_6H_{14}N_2O$		130.19	5
N-nitroso-di-n-butylamine (NDBA)	$C_8H_{18}N_2O$		158.24	3
N-nitrosodiphenylamine (NDPhA)	$C_{12}H_{10}N_2O$		198.22	–
N-nitrosopyrrolidine (NPYR)	$C_4H_8N_2O$		100.10	15
N-nitrosopiperidine (NPIP)	$C_5H_{10}N_2O$		114.15	3.5
N-nitrosomorpholine (NMOR)	$C_4H_8N_2O_2$		116.12	5

UV photolysis may be used to destroy NAs, although few studies have examined which UV wavelengths destroy NAs. Most studies of the destruction of NAs have used sunlight photolysis or UV photolysis [15,16], but the only wavelength used was 254 nm [17], except one study that used different UV wavelengths [9]. It might be useful to study the destruction of NAs by UV photolysis at different wavelengths. The objective of this study is to test the ability of four different UV lamps to degrade NAs under several conditions, with NAs alone in solution or a mix of nine NAs in solution and two different types of water (Milli-Q water and drinking water).

2. Materials and methods

2.1. Reagents

The NDMA, NDEA, NDPA, NDPhA, *N*-nitrosopiperidine (NPIP), NDBA, and mixture of nine NAs were all purchased from Supelco Analytical (Bellefonte, PA, USA) with purities exceeding 98%. The eluent for ultra-performance liquid chromatography coupled with tandem mass spectrometry (UPLC-MS/MS) was prepared with distilled water purchased from Kanto Chemical (Tokyo, Japan). All other reagents used were of analytical grade, used without further purification, and obtained from commercial suppliers.

2.2. UV irradiation

2.2.1. UV lamps

Four UV lamps were used for these experiments: a KrCl excimer lamp with a peak at 222 nm (222 EX; Ushio, Tokyo, Japan, 120W), a low-pressure mercury lamp with a peak at 254 nm (LP; GE/Hitachi, 15W×2), a filtered medium-pressure mercury lamp with the emission range narrowed to 230–270 nm (FMP; Ebara, 456W) by an optical filter (Optical Coatings, Japan), and an XEFL lamp (Ushio) with the emission range narrowed to 220–280 nm. The emission spectrum of each lamp is shown in Fig. 1.

2.2.2. UV irradiance measurements

The UV irradiance of the lamps was calculated using iodide/iodate actinometry [18]. Briefly, 20 mL of the actinometry solution was added to Petri dishes 5.82 cm in diameter, and each dish was exposed to a UV lamp. After an appropriate irradiation period, the absorbance of the actinometry solution was measured to calculate the irradiance.

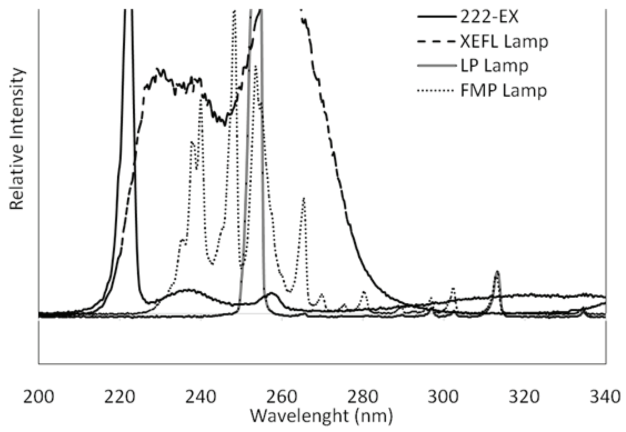


Fig. 1. Emission spectrum of each lamp.

2.2.3. UV irradiation experiment

The stock solution concentration was 2 g/L for the mix of nine NAs and NDBA and 5 g/L for the other NAs. The NAs were dissolved in methanol, except for the NDBA, which was dissolved in dichloromethane. The working solution concentration for UV irradiation was 100 μg/L in water with less than 1% methanol for each NA. First, the stock solution was diluted in methanol (by a dilution factor of 50 or 125) to obtain a 100 mg/L solution in methanol. This solution was then stored in a freezer and used within 1 month. Subsequently, the 100 mg/L solution was diluted in Milli-Q water to get a working solution at 100 μg/L. In addition, to investigate the water matrices, bottled water (Evian) was used. This bottled ground water was chosen as a representative drinking water because it is available commercially worldwide. The 20-mL working solution was poured into 5.82-cm-diameter Petri dishes, and each dish was exposed to a UV lamp at room temperature. A sample of the exposed solution was taken every 5 min for 20 min.

2.2.4. NA measurements

The measurements were made by UPLC-MS/MS which has a detection limit of 1 μg/L for all NAs. The solutions were separated in a BEH C18 column (2.1 × 150 mm, Waters), at a flow rate of 0.2 mL/min with an injection volume of 10 or 30 μL. Table 2 shows the detected ion pairs, retention time, and injection volume for each NA.

3. Results and discussion

3.1. Degradation of the nine NAs in mixed solution

The degradation of the nine NAs in a mixed solution is shown in Figs. 2(a)–(d) for the 222-EX, XEFL, LP, and FMP lamps, respectively. Degradation followed a pseudo-first-order reaction. The degradation rates of the nine NAs in Milli-Q water are shown in Fig. 3. There is no result for NDEA with the FMP lamp due to an analytical error. There were differences according to the type of lamp or compound. The two mercury-free lamps (222-EX and XEFL) performed better than the mercury lamps (LP and FMP) in Milli-Q water. With the 222-EX and XEFL lamps, the degradation rate ranged from 5 to 10 cm^2/J, which was much larger than with the LP lamp. In Milli-Q water, the reaction is dominated by the absorbance of the compound and emission by the lamp at a specific wavelength, because there is no interference by other factors. Therefore, the higher degradation rates with the 222-EX and XEFL could be attributed to the difference in the emission spectra of the two lamps. While the LP lamp emits 254-nm light, the 222-EX and XEFL emit wavelengths of 220–250 nm. NAs generally absorb UV light at shorter wavelengths, with peak absorption at 230–240 nm. The greater overlap in the wavelength ranges of NA absorption, and UV emission would result in greater degradation rates for the 222-EX and XEFL lamps.

Table 2
Analytical conditions for each NA

Compounds	Injection volume (μL)	Ion pairs detected (m/z)		Retention times (min)		
				Average	Minimum	Maximum
NDMA	30	74.90	60.90	3.11	3.05	3.20
NDEA	30	103.00	168.90	6.05	5.98	6.11
NDPA	10	131.00	89.00	6.39	6.33	6.40
NDBA	10	159.00	69.00	6.65	6.64	6.66
NMEA	30	88.90	43.10	5.65	5.55	5.75
NDPhA	10	199.00	75.00	6.60	6.59	6.61
NPYR	30	100.97	87.00	5.85	5.75	5.95
NPIP	30	115.00	103.00	6.10	6.02	6.13
NMOR	30	119.00	55.00	4.53	4.43	4.60

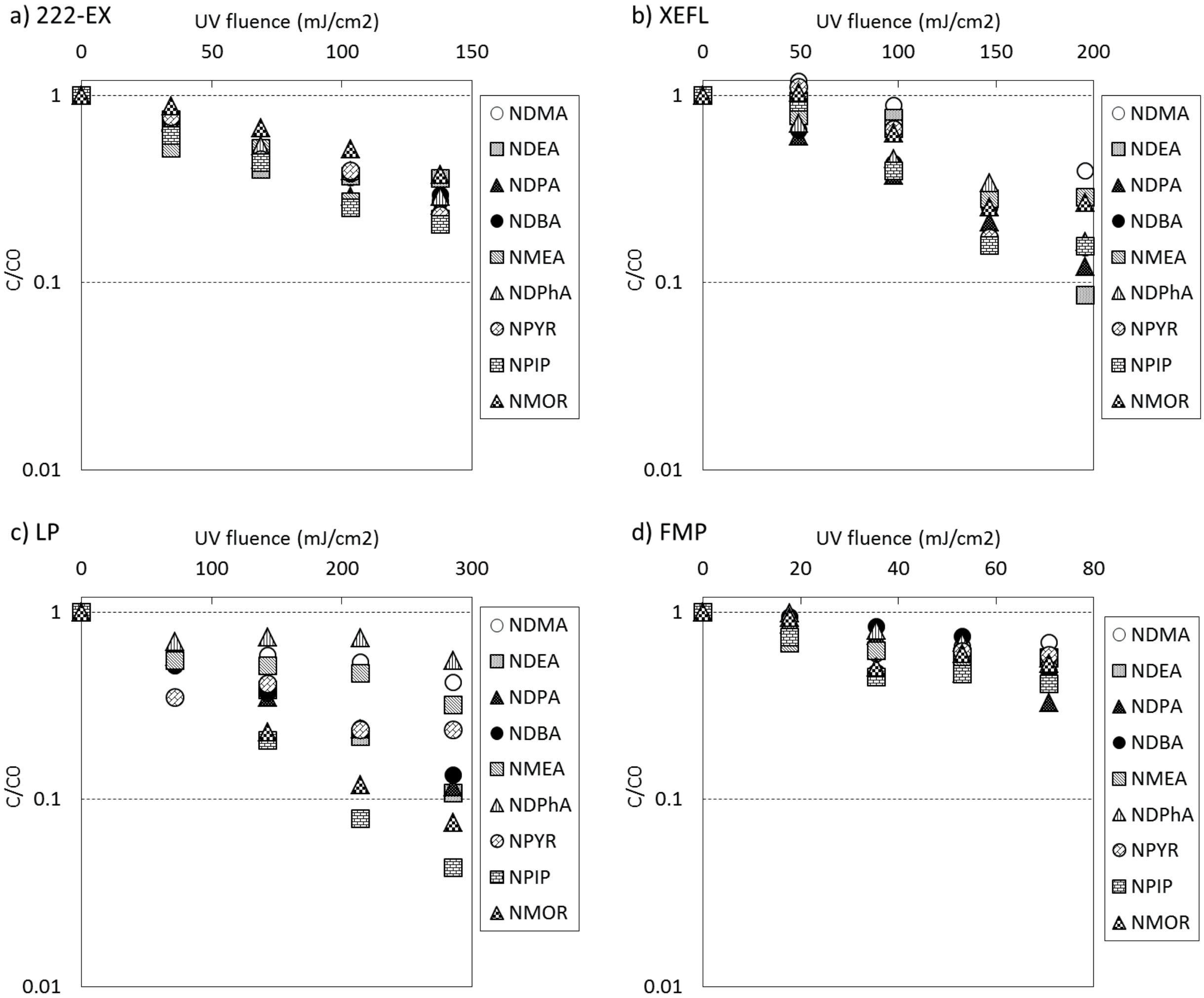


Fig. 2. Degradation of the nine NAs with the a) 222-EX, b) XEFL, c) LP, and d) FMP lamps.

Compared with NDMA, the classic NA, the other NAs were more susceptible to UV light. With the 222-EX lamp, the degradation rate was similar for NDMA and the other NAs. With the XEFL and FMP lamps, the rate was lowest for NDMA and higher for all other NAs. With the LP lamp, the rate was lowest for NDPhA, followed by NDMA and the other NAs. UV cuts the N–N bond at the center of NDMA [19]. The degradation pathways in the other NAs have not been investigated. The reason for the higher degradation rates for the other NAs is not yet known and needs to be pursued.

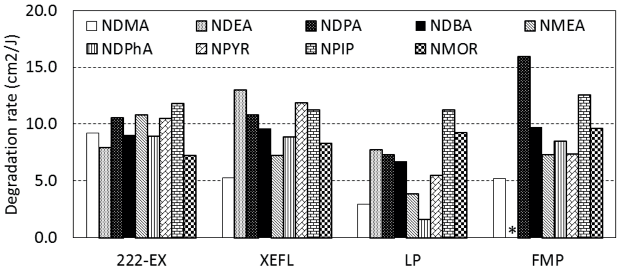


Fig. 3. Degradation rate of each NA with the UV lamps. * No data.

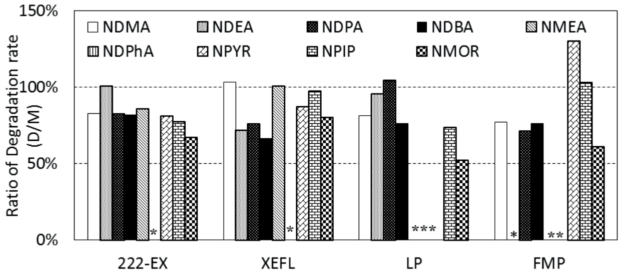


Fig. 4. Comparison of the degradation rates in Milli-Q water (M) and drinking water (D). * No data.

3.2. Impact of interfering substances on degradation

3.2.1. Impact of water matrices

In Milli-Q water, the reaction is dominated simply by the absorbance of the compound and emission by the lamp at a specific wavelength because there is no interference by other factors. Some compounds interfere with the degradation reactions in practical UV treatment systems. Organic matter or nitrate dissolved in water affects the degradation efficiency. These compounds absorb UV light before the light reaches the target NAs. The extent of the interference was investigated experimentally using a solution containing such additives. The bottled water contained about 2.2 mg C/L of Dissolved Organic Carbon (DOC), and 1.1 mg N/L of nitrate. The results are shown in Fig. 4 as the percentage of the rate in Milli-Q water. There are no results for NDPhA for all lamps, NMEA for LP and FMP, and NPYR for LP because the data could not be obtained at an analytical step or a calculation step. Overall, the rate was reduced moderately compared with the rate in Milli-Q water. Even with the bottled water, rates of around 70% were still observed for most of the NAs with all types of UV lamp. Therefore, UV irradiation has potential application in the degradation of NAs in water.

3.2.2. Competition among NAs

In the experiment with the mix of nine NAs, the NAs themselves can interfere with the degradation of a specific NA by preventing the delivery of UV light. To determine the extent of this interference, an experiment was performed using single-compound solutions of NDEA, NDPA, NDBA, and NPIP under the same UV conditions. The other NAs were not used because they were not available commercially as single compounds. Fig. 5 shows the results as the ratio of a single compound to the mixture of nine NAs. Due to errors, there are no results for NPIP with XEFL or NDEA with FMP. The ratio was dependent on the compound and type of lamp. For NPIP, the ratio was close to 100% with the 222-EX, LP, and FMP lamps. For NDPA, the ratio was almost 100% with the 222-EX and XEFL lamps, while it increased to about 200% with the LP lamp. Similar increases were observed for NDEA with 222-EX and LP, and NDBA with 222-EX, XEFL, and LP. Overall, there was a large difference between the degradation of single compounds and that of the mixture of NAs, indicating that practical degradation efficiency may vary in the presence of other NAs. Therefore, the results for the mixture of nine NAs can be used to evaluate practical treatment, while the use of a single compound is recommended to investigate a specific reaction accurately, especially to obtain the quantum yield.

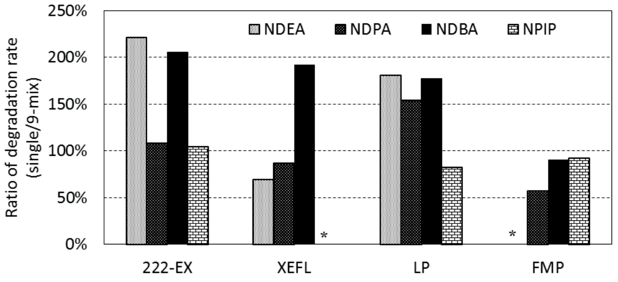


Fig. 5. Comparison of the degradation rates of the mixture of nine NAs and the single compounds. * No data

There were no distinct differences in the absorption spectra of each single NA, as reported [15]. NAs generally have absorption peaks around 230–240 nm, and all four single compounds had peaks in this range. Although one might expect competition to occur similarly for all four compounds, the results differed. Therefore, the differences in Fig. 5 may have been caused not only by competition for UV light delivery but also by interference during the degradation reactions. This point needs further clarification, especially when various NAs are expected to be found in a water sample.

3.3. Effect of structure on degradation efficiency

In this study, nine NAs were subjected to degradation using four different types of UV lamps. As shown in Figs. 2 and 3, the degradation rate in Milli-Q water was 5~10 cm^2/J for all four lamps. Fig. 6 summarizes the results according to the structural differences in the NAs for: (a) non-cyclic and (b) cyclic NAs. For non-cyclic NAs, NDMA, NMEA, NDEA, NDPA, and NDBA are plotted as 1, 1.5, 2, 3, and 4 carbon chains, respectively. For non-cyclic NAs, the degradation rate tended to increase with the number of carbons in the chain. This trend was especially clear where the carbon chain length was 1–2. It appears that smaller NAs are more recalcitrant to UV irradiation. In the case of NDMA, UV cuts the N–N bond at the center of the molecule [19]. For the other NAs, the bond may have been slightly more sensitive to UV irradiation, or another weaker bond may have been cleaved. The trend

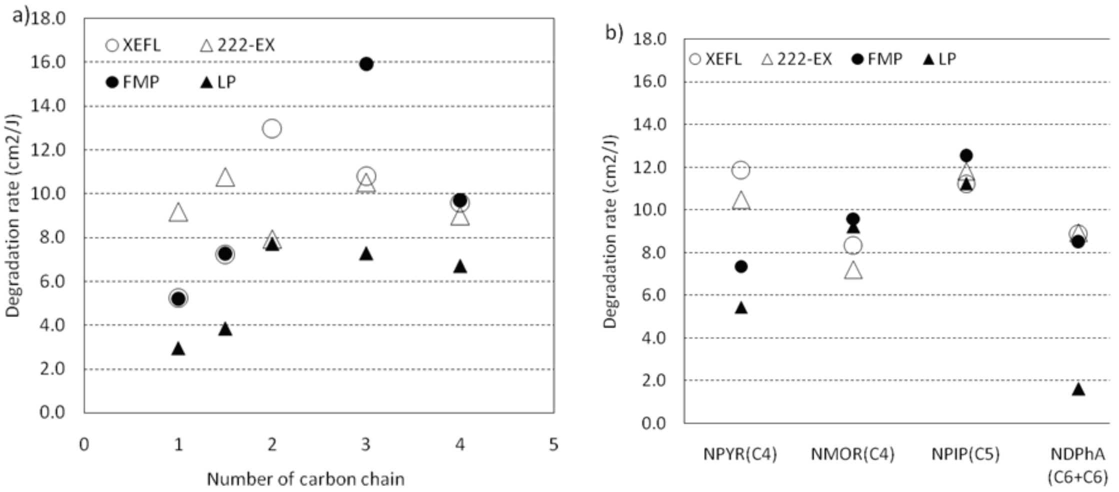


Fig. 6. Degradation-rate summary according to the structural differences of a) non-cyclic NAs and b) cyclic NAs.

was reversed slightly between carbon chain lengths of 3 and 4. The cause of this reversal is unknown and needs further investigation.

NDPhA is the only aromatic NA among the four cyclic NAs in Fig. 6(b) and may follow a different degradation pathway from the other NAs due to its structural difference. Of the other three cyclic NAs, NPIP was the most sensitive to UV degradation. The rate was lower for penta-structure NPYR than for hexa-structure NPIP. This may be due to the number of carbons, as discussed for non-cyclic NAs. Next, the two hexa-structure NAs (NPIP and NMOR) were compared. These two NAs differ by an oxygen atom in the ring. The degradation rate was clearly lower for NMOR than for NPIP. This suggests that the oxygen atom made the compound more refractory to UV degradation. Future studies should examine the degradation pathways of these compounds.

4. Conclusions

This study investigated the degradation of nine NAs using four different types of UV lamp: two mercury UV lamps (LP and FMP) and two mercury-free UV lamps (222-EX and XEFL). All were found to have similar abilities to degrade the nine NAs. Of the nine NAs, the most persistent was NDMA. Therefore, the behavior of NDMA could be a potential indicator of the degradation of all nine NAs in practical water treatment processes.

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